

PATENT  
4249-0112P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: YAO, Kui et al. Conf.: Unassigned  
Appl. No.: 10/680,229 Group: Unassigned  
Filed: October 8, 2003 Examiner: UNASSIGNED  
For: METHOD TO PRODUCE A RELIABLE  
PIEZOELECTRIC THICK FILM ON A SUBSTRATE

L E T T E R

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

January 8, 2004

Sir:

Under the provisions of 35 U.S.C. § 119 and 37 C.F.R. § 1.55(a), the applicant(s) hereby claim(s) the right of priority based on the following application(s):

<u>Country</u>	<u>Application No.</u>	<u>Filed</u>
SINGAPORE	200206099-4	October 9, 2002


A certified copy of the above-noted application(s) is(are) attached hereto.

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Respectfully submitted,

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JMS:trb  
4249-0112P

Attachment(s)

(Rev. 09/30/03)

4249,0112P  
10/680,229  
October 8, 2003  
Kui YAO et al.  
BSKB  
(703) 205-8000

**REGISTRY OF PATENTS  
SINGAPORE**


This is to certify that the annexed is a true copy of specification as filed for the following Singapore patent application.

Date of Filing : 09 OCTOBER 2002

Application Number : 200206099-4

Applicant(s) /  
Proprietor(s) of  
Patent : INSTITUTE OF MATERIALS RESEARCH  
AND ENGINEERING

Title of Invention : METHOD TO PRODUCE A RELIABLE  
PIEZOELECTRIC THICK FILM ON A  
SUBSTRATE



SHARMAINE WU (Ms)  
Assistant Registrar  
for REGISTRAR OF PATENTS

INTELLECTUAL PROPERTY OFFICE OF SINGAPORE  
REQUEST FOR THE GRANT OF A PATENT UNDER  
SECTION 25

101101

\* denotes mandatory fields

1. YOUR REFERENCE\*

A2-0426 PYK/rsa

2. TITLE OF  
INVENTION\*

METHOD TO PRODUCE A RELIABLE PIEZOELECTRIC THICK FILM  
ON A SUBSTRATE

3. DETAILS OF APPLICANT(S)\* (see note 3)

Number of applicant(s)

1

(A) Name

INSTITUTE OF MATERIALS RESEARCH AND ENGINEERING

Address

3 RESEARCH LINK  
SINGAPORE 117602

State

Country

SG

☒

For corporate applicant

☐

For individual applicant

State of incorporation

State of residency

Country of incorporation

SG

Country of residency

☐

For others (please specify in the box provided below)

(B) Name

Address

State

Country



☐ For corporate applicant

☐ For individual applicant

State of incorporation

State of residency

Country of incorporation

Country of residency

☐ For others (please specify in the box provided below)

(C) Name

Address

State

Country

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State of incorporation

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Further applicants are to be indicated on continuation sheet 1

4. DECLARATION OF PRIORITY (see note 5)

A. Country/country designated

DD MM YYYY

File number

Filing Date

B. Country/country designated

DD MM YYYY

File number

Filing Date

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Further details are to be indicated on continuation sheet 6

5. INVENTOR(S)\* (see note 6)

A. The applicant(s) is/are the sole/joint inventor(s)

Yes

☐

No

☒

09 OCT 2002  
200206099-4

B. A statement on Patents Form 8 is ~~will be~~ furnished

Yes

☒

No

☐

6. CLAIMING AN EARLIER FILING DATE UNDER (see note 7)

☐

section 20(3)

☐

section 26(6)

☐

section 47(4)

Patent application number

DD MM YYYY

Filing Date

Please mark with a cross in the relevant checkbox provided below  
(Note: Only one checkbox may be crossed.)

☐

Proceedings under rule 27(1)(a)

DD MM YYYY

Date on which the earlier application was amended

☐

Proceedings under rule 27(1)(b)

7. SECTION 14(4)(C) REQUIREMENTS (see note 8)

Invention has been displayed at an international exhibition.

Yes

☐

No

☒

8. SECTION 114 REQUIREMENTS (see note 9)

The invention relates to and/or used a micro-organism deposited for the purposes of disclosure in accordance with section 114 with a depository authority under the Budapest Treaty.

Yes

☐

No

☒

9. CHECKLIST\*

(A) The application consists of the following number of sheets

i. Request

5

Sheets

ii. Description

10

Sheets

iii. Claim(s)

4

Sheets

iv. Drawing(s)

1

Sheets

v. Abstract  
(Note: The figure of the drawing, if any, should accompany the abstract)

1

Sheets

Total number of sheets

21

Sheets

(B) The application as filed is accompanied by:

☐

Priority document(s)

☐

Translation of priority document(s)

☒

Statement of inventorship  
& right to grant

☐

International exhibition certificate

**10. DETAILS OF AGENT (see notes 10, 11 and 12)**

Name

Firm

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**11. ADDRESS FOR SERVICE IN SINGAPORE\* (see note 10)**

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Building Name

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Postal Code

038989

**12. NAME, SIGNATURE AND DECLARATION (WHERE APPROPRIATE) OF APPLICANT OR AGENT\* (see note 12)**

(Note: Please cross the box below where appropriate.)

☒

I, the undersigned, do hereby declare that I have been duly authorised to act as representative, for the purposes of this application, on behalf of the applicant(s) named in paragraph 3 herein.

PATSY KOH



Name and Signature

DD MM YYYY

9/10/2002

#### NOTES:

1. This form when completed, should be brought or sent to the Registry of Patents together with the rest of the application. Please note that the filing fee should be furnished within the period prescribed.
2. The relevant checkboxes as indicated in bold should be marked with a cross where applicable.
3. Enter the name and address of each applicant in the spaces provided in paragraph 3.  
Where the applicant is an individual
  - Names of individuals should be indicated in full and the surname or family name should be underlined.
  - The address of each individual should also be furnished in the space provided.
  - The checkbox for "For individual applicant" should be marked with a cross.  
Where the applicant is a body corporate
  - Bodies corporate should be designated by their corporate name and country of incorporation and, where appropriate, the state of incorporation within that country should be entered where provided.
  - The address of the body corporate should also be furnished in the space provided.
  - The checkbox for "For corporate applicant" should be marked with a cross.  
Where the applicant is a partnership
  - The details of all partners must be provided. The name of each partner should be indicated in full and the surname or family name should be underlined.
  - The address of each partner should also be furnished in the space provided.
  - The checkbox for "For others" should be marked with a cross and the name and address of the partnership should be indicated in the box provided.
4. In the field for "Country", please refer to the standard list of country codes made available by the Registry of Patents and enter the country code corresponding to the country in question.
5. The declaration of priority in paragraph 4 should state the date of the previous filing, the country in which it was made, and indicate the file number, if available. Where the application relied upon in an International Application or a regional patent application e.g. European patent application, one of the countries designated in that application [being one falling under section 17 of the Patents Act] should be identified and the country should be entered in the space provided.
6. Where the applicant or applicants is/are the sole inventor or the joint inventors, paragraph 5 should be completed by marking with a cross the 'YES' checkbox in the declaration (A) and the 'NO' checkbox in the alternative statement (B). Where this is not the case, the 'NO' checkbox in declaration (A) should be marked with a cross and a statement will be required to be filed on Patents Form 8.
7. When an application is made by virtue of section 20(3), 26(6) or 47(4), the appropriate section should be identified in paragraph 6 and the number of the earlier application or any patent granted thereon identified. Applicants proceeding under section 26(6) should identify which provision in rule 27 they are proceeding under. If the applicants are proceeding under rule 27(1)(a), they should also indicate the date on which the earlier application was amended.
8. Where the applicant wishes an earlier disclosure of the invention by him at an International Exhibition to be disregarded in accordance with section 14(4)(c), then the 'YES' checkbox at paragraph 7 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross.
9. Where in disclosing the invention the application refers to one or more micro-organisms deposited with a depository authority under the Budapest Treaty, then the 'YES' checkbox at paragraph 8 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross. Attention is also drawn to the Fourth Schedule of the Patents Rules.
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11. In the event where an individual is appointed as an agent, the sub-field "Name" under "DETAILS OF AGENT" must be completed by entering the full name of the individual. The sub-field "Firm" may be left blank. In the event where a partnership/body corporate is appointed as an agent, the sub-field "Firm" under "DETAILS OF AGENT" must be completed by entering the name of the partnership/body corporate. The sub-field "Name" may be left blank.
12. Attention is drawn to sections 104 and 105 of the Patents Act, rules 90 and 105 of the Patents Rules, and the Patents (Patent Agents) Rules 2001.
13. Applicants resident in Singapore are reminded that if the Registry of Patents considers that an application contains information the publication of which might be prejudicial to the defence of Singapore or the safety of the public, it may prohibit or restrict its publication or communication. Any person resident in Singapore and wishing to apply for patent protection in other countries must first obtain permission from the Singapore Registry of Patents unless they have already applied for a patent for the same invention in Singapore. In the latter case, no application should be made overseas until at least 2 months after the application has been filed in Singapore, and unless no directions had been issued under section 33 by the Registrar or such directions have been revoked. Attention is drawn to sections 33 and 34 of the Patents Act.
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**METHOD TO PRODUCE A RELIABLE PIEZOELECTRIC THICK FILM  
ON A SUBSTRATE**

Technical Field

5           This invention relates to piezoelectric devices and, more particularly, methods of producing such devices. In particular, the invention relates to a method of fabricating a piezoelectric device involving printing a paste containing piezoelectric ceramic material onto a substrate so as to form a piezoelectric ceramic thick film on the substrate.

10

Background of the Invention

          A number of materials are known to exhibit a piezoelectric effect, being the generation of electricity under mechanical stress. Conversely, such materials may undergo a degree of physical deformation when subjected to an electrical field. These piezoelectric manifestations are utilised in a number of "piezoelectric" devices which generate either an electrical signal caused by pressure (used as sensors) or deformation by exposure to an electrical field (used as actuators). This piezoelectric effect is the result of the anisotropy of the crystalline structure (eg. Quartz, ferroelectric lead zirconate titanate (PZT) ceramics).

20

          Ferroelectric ceramics, such as PZT, are now used in diverse technological applications where the unique piezoelectric (and ferroelectric) properties of these materials can be exploited. Piezoelectric devices have been made by forming PZT thin films on a substrate where the film thickness typically ranges from about 0.1 to 1.0  $\mu\text{m}$ . These devices have use in microelectronic and micro-systems applications.

25

          Piezoelectric devices have also been made of bulk piezoelectric ceramics. The bulk piezoelectric ceramics are formed by the sintering of discrete ceramic particles without a substrate.

30

          There has, over recent years, been an increasing interest in piezoelectric ceramic thick film technology in relation to applications that combine device



performance requirements approaching those of bulk piezoelectrics but with the miniature size scale required for use in microelectronic packages. The term "thick film" in the present context means a film having a thickness of between about 10  $\mu\text{m}$  and 100  $\mu\text{m}$ .

5           Thick layers of piezoelectric ceramic material are advantageous in that larger actuating forces, or (in the case of the reverse effect) larger sensing signals, may be generated (when compared to thin-film devices).

          It is perceived that piezoelectric ceramic (eg PZT) thick films will have applications in various devices including chemical sensors, torque and pressure  
10       sensors, pyroelectric arrays, buzzers, micro-pumps, high frequency ultrasonic transducers, mass microbalances, microactuators, microtransducers, micro-accelerometers, micro-strain gauges and micro-resonators.

          Various technologies are relatively well known for the formation of thin film piezoelectric ceramics and bulk ceramics. However, the integration of  
15       piezoelectric ceramic thick films into micro-electronic packages poses a number of technical difficulties relating primarily to processing and integration compatibility with the underlying substrate.

          In recent years, it has been discovered that the deposition of piezoelectric ceramic powders (in paste form), by printing the paste onto the substrate,  
20       followed by annealing (ie firing), is an efficient method to form a piezoelectric thick film of about 10 $\mu\text{m}$  to 100  $\mu\text{m}$  on a substrate. This annealing step is done so as to sinter the particles together to form a cohesive film with suitable electrical and mechanical properties.

          However, the processing temperature for sintering piezoelectric ceramic,  
25       such as PZT, is as high as 1,200°C (for several hours). Temperatures of this magnitude are not compatible with many of the substrates, including electroded silicon. This is because at such elevated temperatures, lead diffuses into the bottom electrode and silicon substrate, and thus the substrate is damaged. Accordingly, in the formulation of piezoelectric ceramic thick films on silicon  
30       substrates, the maximum allowable firing (annealing) temperature is between about 900°C and about 1,000°C.

Certain sintering aids for PZT and other piezoelectric ceramic thick films have been developed. Sintering aids for PZT which have been developed are generally low-melting metal oxide powders. The addition of these metal oxide powders relies, at least in part, on liquid-phase sintering for densification of the ceramic. The presence of such metal oxide powder enables sintering to occur at lower temperatures. The chosen metal oxide powder is typically added to the PZT powder through mechanical mixing and this is followed by the further addition of an organic carrier (or vehicle). The powders and the organic carrier are well mixed to form a paste. This paste is then, typically, screen-printed onto the substrate as a wet film. This wet film is then dried and the layered substrate then undergoes annealing at temperatures of between about 800°C and 1,000°C. The above sintering aids (eg metal oxide powders) help to keep the annealing temperature at a level which inhibits (or reduces) diffusion of lead into the silicon substrate, and reduces the damage of the bottom electrode and the substrate.

However, the mechanical mixing method of the piezoelectric ceramic powder with the metal oxide powder, which is added as the sintering aid, results in a significant lack of homogeneity in the distribution of the metal oxide powder throughout the PZT powder in the as-deposited film. In turn, this lack of homogeneity results in a non-uniform distribution of the liquid-phase of the added sintering aids in the sintering process. This adversely affects the stability of the resultant thick film and the piezoelectric properties of the film. In comparison with bulk ceramic, this problem is particularly serious for the thick film in which a high sintering temperature and long sintering time are not allowed in order to minimise the damage of the bottom electrode and the substrate.

Accordingly, the present invention is directed towards a method of producing a piezoelectric thick film on a substrate with improved uniform distribution of the glass-bonding phase in the piezoelectric ceramic materials and, therefore, having more reliable piezoelectric performance.

Throughout this specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of

elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Any discussion of documents, acts, materials, devices, articles or the like, which has been included in the present specification, is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

## 10 Summary of the Invention

According to a first aspect of this invention, there is provided a method of producing a piezoelectric ceramic thick film on a substrate, said method comprising:

- providing a piezoelectric ceramic material in powder form;
- 15 • forming a liquid mixture by mixing the powdered material with a liquid phase precursor of a metal oxide of low-melting point, said precursor being adapted to decompose, upon subsequent annealing, into the metal oxide;
- drying the liquid mixture to form a precipitate;
- 20 • milling the precipitate to form a powdered precipitate;
- adding an organic carrier to the powdered precipitate;
- further milling the precipitate to form a paste;
- depositing a layer of the paste, as a wet film, onto the substrate; and
- 25 • annealing the layered substrate at a temperature and for a time sufficient to cause transformation of the paste into the thick film.

The piezoelectric ceramic material may be any inorganic ceramic material which exhibits the piezoelectric effect, such as the ferroelectric ceramics. A preferred ferroelectric ceramic is lead zirconate titanate (PZT). Other ferroelectric

ceramics which may be used include  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{Pb}(\text{Mg,Nb})\text{O}_3$ ,  $\text{Pb}(\text{Zr,Nb})\text{O}_3$ ,  $\text{Pb}(\text{Ni,Nb})\text{O}_3$ ,  $\text{KNbO}_3$ ,  $\text{KTaO}_3$ ,  $\text{NaNbO}_3$ ,  $\text{LiNbO}_3$ .

The metal oxide may be any metal oxide which promotes the sintering process of the piezoelectric ceramic at a lower temperature. Preferably, the  
5 metal oxide is one which is adapted to form a glass phase upon annealing at elevated temperature. Suitable metal oxides include one or more of  $\text{Li}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$ .

Preferably, the liquid phase precursor is a combination of the liquid phase precursors of  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$ . The liquid phase precursor of  $\text{Li}_2\text{O}$  is preferably  
10 lithium ethoxide dissolved in ethanol. The liquid phase precursor of  $\text{Bi}_2\text{O}_3$  is preferably bismuth nitrate dissolved in acetic acid. These liquid phase precursors are mixed to form a Li-Bi acetic acid solution (which is transparent).

The powdered piezoelectric ceramic material (such as PZT) may be added to this Li-Bi acetic acid solution. However, it is preferred that the  
15 powdered material is in the form of a suspension. This suspension may consist of the powder suspended in ethanol. The powdered material is thereby mixed with the liquid agent by combining the powder suspension with the Li-Bi acetic acid solution to form the liquid mixture. The liquid mixture, obtained by mixing the powder suspension with the Li-Bi acetic acid solution, has a greater degree  
20 of homogeneity than would otherwise be obtained by simply mixing the powdered material with the Li-Bi acetic acid solution.

Alternatively, the metal oxide may be  $\text{PbO}$  in which case the liquid phase precursor would be a solution of lead acetate. In this case, the above step would involve this lead acetate solution instead of the Li-Bi acetic acid solution.

25 It is preferable that the powdered ceramic material in the suspension is fine-grained having, for instance, an average grain size below about  $1.0\mu\text{m}$ . It is particularly preferred that the average grain size is about  $0.5\mu\text{m}$ .

The quantity of the liquid phase precursor of the metal oxide will be quite small as only a small amount of glass phase is desired. If too much glass phase  
30 is produced, the piezoelectric performance of the resultant thick film will be significantly weakened. It has been found that the preferred doping amount of

the metal oxide (eg  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$ ) is between about 1 to about 5 weight percent of the abovementioned paste.

The abovementioned liquid mixture should be dried at an elevated temperature so as to form a dried precipitate. Preferably, the drying procedure is carried out between about 75-150°C for about 1 to 10 hours. The dried precipitate is then formed into a powder, preferably by milling with a ball mill. The organic carrier is then added and the ball milling process is continued so as to form a paste. This results in the metal oxide dopant being homogeneously distributed throughout the powdered piezoelectric ceramic material. By using the liquid phase precursors of the metal oxide (eg.  $\text{Li}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$ , or  $\text{PbO}$ ), these precursors form a coating around the grains of powder resulting in a highly homogenous distribution of the dopant material.

The main purpose of the organic carrier is so as to give the dried precipitate a pasty nature. This carrier can be any suitable organic solvent. Suitable solvents have been found to include ethyl cellulose, terpineol, ESL400 organic vehicle and ethanol. A particularly preferred carrier is ESL400.

The abovementioned paste is then deposited onto a surface of the substrate as a wet film. This deposition is typically achieved by any suitable printing process, such as a screen printing process.

The wet film may then be dried at room temperature or at an elevated temperature for a shorter time, for instance at a temperature of about 150°C.

The printing and drying process may be repeated to achieve an increased thickness.

The layered substrate is then generally annealed at a temperature of between about 800°C to about 1000°C. Temperatures in the range of about 820°C to about 950°C are particularly preferred. The layered substrate will be subjected to such annealing for a period of time of between about 10 min to a few hours.

Prior to this annealing step, an isostatic pressure may be applied to the film. This tends to improve the green density (ie the density before final annealing or sintering) of the film and to enhance, during the annealing step, the bonding effect of the dopant metal oxide.

The relevant substrate may be silicon (eg a Si wafer). The silicon substrate may also have a coating of platinum onto which the abovementioned paste is deposited. This platinum coating may be applied by sputtering.

5 In order to enhance the piezoelectric properties of the thick film, the film will typically undergo a polarisation step. This helps to achieve good piezoelectric properties of the thick film.

10 In order for the piezoelectric effect to be utilised, the above-mentioned device needs to incorporate means by which an electric field may either be applied or detected. Therefore, electrodes are typically placed across the thick film. Accordingly, the above method may include additional steps such as the formation of a metal electrode material on the thick film. This metal electrode may be formed of silver and the electrode may be deposited on the thick film by printing (eg screen printing) processes. The layered substrate may then be fired so as to form the electrode.

15 In order that the present invention may be more clearly understood, preferred forms of the invention will be described with reference to the following drawings and examples.

#### Brief Description of the Drawing

20 Figure 1 schematically illustrates the processing flow for preparing the PZT piezoelectric thick film according to example 1(below).

#### Detailed Description of the Invention

25 A preferred embodiment of the method of this invention is described below by reference to the following examples. These examples are illustrations only of a preferred embodiment of the invention. The invention is not, however, limited to the features specified in these examples.

#### Example 1

30 In example 1, bismuth oxide and lithium oxide were selected as the sintering aids.

An ethanol solution of 0.003972 mol lithium ethoxide was mixed with 0.24g of glacial acetic acid by stirring. 0.003972 mol of bismuth nitrate pentahydrate was dissolved in 14g of glacial acetic acid at a temperature of 75°C. After cooling down to room temperature, the bismuth nitrate solution was  
5 mixed with the lithium ethoxide solution at a temperature of 65°C. The mixed solution was the transparent precursor solution containing the Bi and Li elements.

97.5g of lead zirconate titanate (PZT) powders with an average grain size of 0.5  $\mu\text{m}$  was dispersed in 70g of ethanol by stirring with an ultrasonic vibration.  
10 After the Bi-Li precursor solution was mixed with the PZT suspension, the mixture was dried at 78°C overnight to obtain a precipitate of the PZT powders with the added Bi and Li elements. The precipitate was milled in an agate ball for 3 hours at a speed of 300 rpm, and then 32g of ESL400 binder was added and the ball-milling process was continued for another 3 hours to form the PZT paste  
15 with a suitable viscosity and rheology for the following printing process.

A 4-inch single crystal silicon wafer was selected as the substrate on which the PZT paste was to be deposited. The 4-inch Si wafer was (100) oriented, and was coated by a sputtering process with a Pt layer of 0.5 to 1  $\mu\text{m}$  in thickness and an intermediate Ti layer having a thickness of 0.05  $\mu\text{m}$ . With a  
20 screen printer, the PZT paste was forced by a squeegee through the open pattern in a stencil screen and deposited onto the Pt-coated Si wafer. The wet film was dried at 150°C for 3 minutes, and the printing and drying process was repeated twice to increase the thickness of the films.

The dried film was first fired in air at a temperature of 400°C for 10 hours  
25 to remove the organic binders.

The Si substrate with the PZT film was loaded into a flexible soft plastic bag with good tenacity. The soft plastic bag was evacuated using a vacuum pump and then the bag was hermetically packaged. The package was completely immersed in a liquid medium in an isostatic pressure machine, and  
30 an isostatic pressure of 3500kg/cm<sup>2</sup> was applied and held for 10 minutes.

The pressed film was fired at a temperature of 925°C in air for 30 minutes.

A commercial silver paste from Dupont was deposited by screen printing process on the top of the fired PZT film, and fired at 520°C in air for 10 minutes to form the top electrode for the PZT film.

5 An electrical field of 150 kV/cm was applied to the PZT thick film for poling.

### Example 2

In example 2, lead oxide was selected as the sintering aid.

10 0.02298 mol lead acetate trihydrate was dissolved in 40g of acetic acid at an elevated temperature of 105°C.

97.5g of PZT powders with an average grain size of 0.5  $\mu\text{m}$  was dispersed in 70g of ethanol by stirring with an ultrasonic vibration. After the lead acetate precursor solution was mixed with the PZT suspension, the suspension was dried at 78°C for 1 hour, and then 110°C for 2 hours, and finally at 78°C  
15 overnight to form a precipitate of the PZT powders with the added Pb element. The dried precipitate was milled in an agate ball for 3 hours at a speed of 300 rpm, and then 34g of ESL400 binder was added. The ball-milling process was continued for another 3 hours to get the PZT paste with a suitable viscosity and rheology for the printing process.

20 The subsequent printing process and poling process were the same as for Example I.

The piezoelectric ceramic thick films formed according to the methods of the abovementioned invention have porous features and exhibit reliable  
25 piezoelectric responses. The stable piezoelectric vibration module of the film under AC electrical stimulation was observed with a laser scanning vibrometer. They possess a very high piezoelectric voltage constant ( $g^{33}$ ) of 32 mmV/N. This is largely due to the porous nature of the films and their small dielectric constant. The piezoelectric voltage constant for such films is generally higher  
30 than that of typical bulk piezoelectric ceramics. This makes these thick films very attractive as integrated piezoelectric sensors for a variety of applications.



Accordingly, the abovementioned invention provides an efficient way of forming piezoelectric ceramic thick films having reliable performance characteristics at relatively low temperatures. It also enables piezoelectric ceramic thick films to be formed on substrates, such as silicon and glass, for which excessively high temperatures (eg in excess of 1000°C) is not technically feasible.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as described herein without departing from the spirit or scope of the invention. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive.

## Claims

The claims defining this invention are as follows:

1. A method of producing a piezoelectric ceramic thick film on a substrate, said method comprising:
  - 5       • providing a piezoelectric ceramic material in powder form;
  - forming a liquid mixture by mixing the powdered material with a liquid phase precursor of a metal oxide of low-melting point, said precursor being adapted to decompose, upon subsequent annealing, into the metal oxide;
  - 10       • drying the liquid mixture to form a precipitate;
  - milling the precipitate to form a powdered precipitate;
  - adding an organic carrier to the powdered precipitate;
  - further milling the precipitate to form a paste;
  - depositing a layer of the paste, as a wet film, onto the substrate;
  - 15       and
  - annealing the layered substrate at a temperature and for a time sufficient to cause transformation of the paste into the thick film.
2. A method according to claim 1, wherein the piezoelectric ceramic material is an inorganic ceramic material which exhibits the piezoelectric effect.
- 20 3. A method according to claim 2, wherein the piezoelectric ceramic material is lead zirconate titanate (PZT).
4. A method according to claim 1, wherein the metal oxide is adapted to form a glass phase upon annealing at elevated temperature.
5. A method according to claim 4, where in the metal oxide is selected from
  - 25       one or more of  $\text{Li}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$ .
6. A method according to claim 5, wherein the liquid phase precursor is a combination of the liquid phase precursors of  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$ .
7. A method according to claim 5 or claim 6, wherein the liquid phase precursor of  $\text{Li}_2\text{O}$  is lithium ethoxide dissolved in ethanol.

8. A method according to claim 5 or claim 6, wherein the liquid phase precursor of  $\text{Bi}_2\text{O}_3$  is bismuth nitrate dissolved in acetic acid.
9. A method according to any one of claims 6 to 8, wherein the liquid phase precursors of  $\text{Li}_2\text{O}$  and  $\text{Bi}_2\text{O}_3$  are mixed to form a Li-Bi acetic acid solution.
10. A method according to claim 5, wherein the metal oxide is  $\text{PbO}$  and the liquid phase precursor is a solution of lead acetate.
11. A method according to any one of claims 1 to 10, wherein the powdered piezoelectric material is in the form of a suspension in ethanol.
12. A method according to claim 11, wherein the powdered piezoelectric material is fine-grained having an average grain size of below about  $1.0\mu\text{m}$ .
13. A method according to claim 12, wherein the average grain size is about  $0.5\mu\text{m}$ .
14. A method according to any one of claims 1 to 13, wherein the total amount of the metal oxide in the thick film is between about 1% and 5%, by weight.
15. A method according to claim 11, wherein the suspension is mixed with the Li-Bi acetic acid solution, or the lead acetate solution, to form a liquid mixture.
16. A method according to claim 15, wherein the liquid mixture is dried at an elevated temperature to form a dried precipitate.
17. A method according to claim 16, wherein the liquid mixture is dried at a temperature between about  $75^\circ\text{C}$  and  $105^\circ\text{C}$  for up to 10 hours.
18. A method according to claim 16 or claim 17, wherein the dried precipitate is formed into a powdered precipitate.
19. A method according to claim 18, wherein the powdered precipitate is formed by milling the dried precipitate with a ball mill.
20. A method according to claim 18 or claim 19, wherein an organic carrier is added to the powdered precipitate.

21. A method according to claim 20, wherein the organic carrier is selected from one or more of ethyl cellulose, terpineol, and ESL 400 organic binder.
22. A method according to claim 21, wherein the organic carrier is ESL 400 organic binder.
23. A method according to any one of claims 18 to 22, wherein the powdered precipitate and organic carrier are milled to form a paste.
24. A method according to claim 23, wherein the paste is deposited onto a surface of the substrate, by a printing process, as a wet film.
25. A method according to claim 24, wherein the printing process is a screen printing process.
26. A method according to any one of claims 1 to 25, wherein, prior to annealing, the layered substrate is dried.
27. A method according to any one of claims 1 to 25, wherein, prior to annealing, an isostatic pressure is applied to the film.
28. A method according to claim 26, wherein the drying temperature is between about 20°C and about 175°C.
29. A method according to any one of claims 1 to 28 wherein the layered substrate is annealed at a temperature of between about 800°C and about 1000°C.
30. A method according to claim 29, wherein the annealing is conducted for between about 10 minutes and about 4 hours.
31. A method according to any one of claims 1 to 30, wherein the substrate is formed of silicon.
32. A method according to any one of claims 1 to 31, wherein the surface of the substrate has a coating of platinum and the paste is deposited on this platinum coating.
33. A method according to any one of claims 1 to 32, wherein a metal electrode is formed on the piezoelectric ceramic thick film.

- 34. A method according to claim 33, wherein the metal is silver and the electrode material is deposited on the film by a screen printing process.
- 35. A method according to claim 34, wherein the layered substrate is fired at elevated temperature to form the electrode.
- 5 36. A method of producing a piezoelectric ceramic thick film on a substrate, said method being substantially as hereinbefore described with reference to Figure 1 and Example 1 or to Example 2.
- 37. A substrate having a piezoelectric ceramic thick film thereon, formed according to the method of any one of claims 1 to 36.
- 10 38. A piezoelectric sensor or actuator having a piezoelectric ceramic thick film, wherein said thick film has been formed on said substrate according to the method of any one of claims 1 to 36.

Abstract

**Method to Produce a Piezoelectric Thick Film on a Substrate**

5 A method of producing a piezoelectric ceramic thick film on a substrate, said method comprising:

10 providing a piezoelectric ceramic material in powder form; forming a liquid mixture by mixing the powdered material with a liquid phase precursor of a metal oxide of low-melting point, said precursor being adapted to decompose, upon subsequent annealing, into the metal oxide; drying the liquid mixture to form a precipitate; milling the precipitate to form a powdered precipitate; adding an organic carrier to the powdered precipitate; further milling the precipitate to form a paste; depositing a layer of the paste, as a wet film, onto the substrate; and annealing the  
15 layered substrate at a temperature and for a time sufficient to cause transformation of the paste into the thick film.

[Figure 1]

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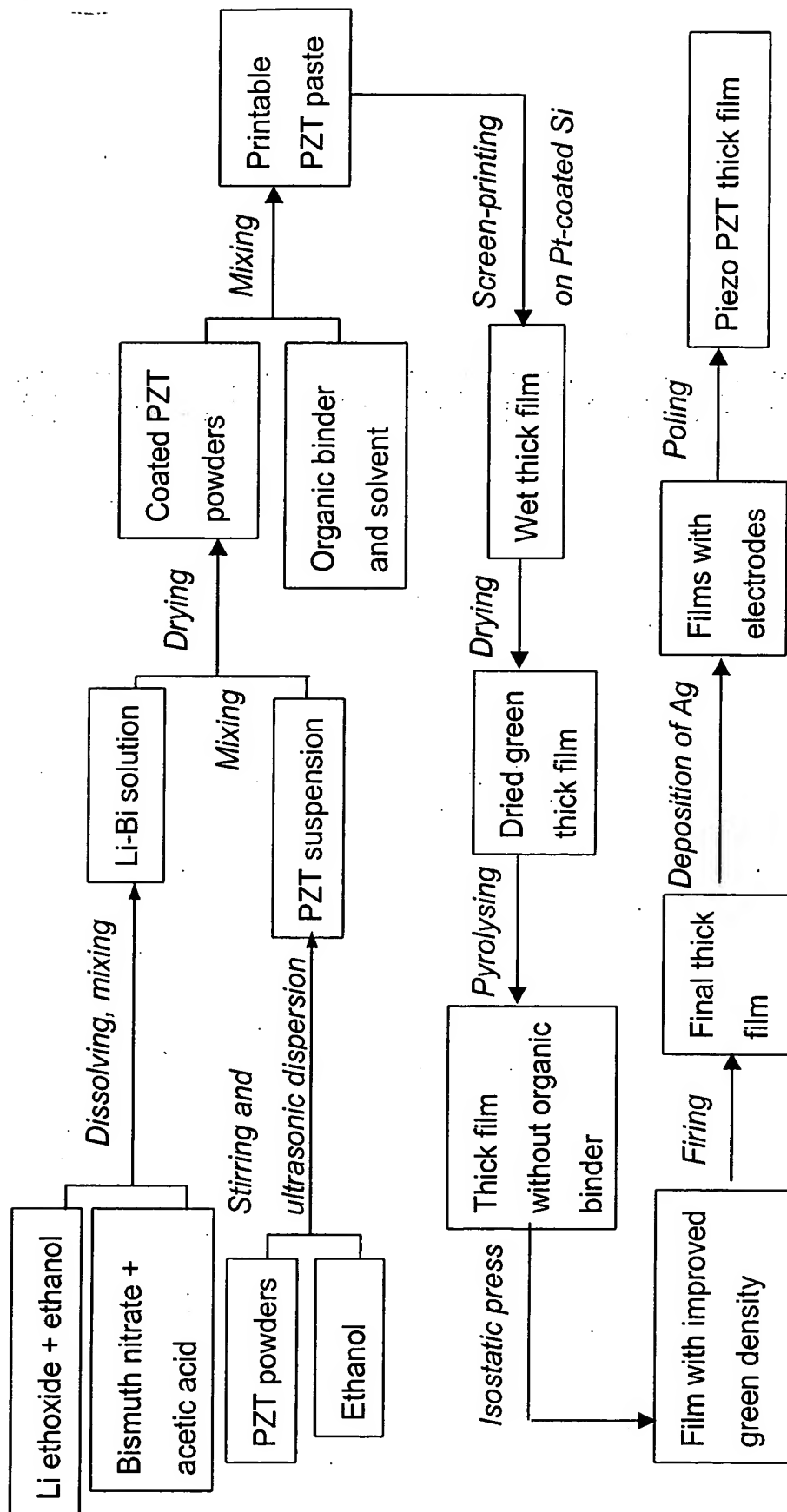


Figure 1